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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Highlights of a recent international conference are presented. The conference, which combined the XX Colloquium Spectroscopicum Internationale and the 7th International Conference on Atomic Spectroscopy, was held in Czechoslovakia from August 30 to Sept. 8, 1977. Although the meeting covered a number of facets of analytical chemistry and spectroscopy, this report emphasizes those parts dealing with atomic spectroscopy. In the report, trends in this field are identified and important new findings related.		

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REPORT ON COMBINED MEETING OF THE  
XX COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE AND (20th) AND  
7TH INTERNATIONAL CONFERENCE ON ATOMIC SPECTROSCOPY (7th).

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From August 8 through September 7, 1977, a combined meeting between the XX Colloquium Spectroscopicum Internationale and the 7th International Conference on Atomic Spectroscopy was held in Czechoslovakia. The conference was unusual in its format in that it consisted of two parts. The first part, attended by all conferees, was held in Prague, Czechoslovakia from August 30 to September 3, 1977. In this principal part of the international meeting, a large number of topics were covered, including atomic spectroscopy, x-ray fluorescence, mass spectrometry, microprobe analysis, vibrational spectroscopy, NMR spectroscopy, radio-analytical methods, Mössbauer spectroscopy, Auger spectroscopy, electron spectroscopy, and the observation of phonons in solids. Because of the large number of individuals attending this conference (over 1200), as many as 13 sessions were held simultaneously, making it difficult to obtain an overall feeling for the breadth of topics being discussed. In this report, I will deal only with important aspects of atomic spectroscopy which were covered during this series of sessions, since those bear most directly on our efforts being supported by ONR.

Following this principal congress, six special-topic "mini-symposia" were held at various locations throughout Czechoslovakia. Of greatest interest to individuals involved in atomic spectroscopy were symposium 1 on "optimization of spectrochemical methods", symposium 2 on "spectrochemical analysis of metals", and symposium 3 on "electrothermal atomization processes in atomic absorption spectroscopy". In a later part of this report, highlights of symposium 3 will be related.

Overall, the principal congress and symposium 3 were well-organized, located in settings conducive to scientific exchange and well-attended by individuals from throughout the world. In contrast to most previous conferences, the location of this meeting behind the Iron Curtain made it possible for many

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eastern European and Russian scientists to attend, thereby affording an opportunity for interchange which seldom arises. Unfortunately, few scientists from the United States were able to attend and it is hoped that this report will provide a useful overview of the proceedings.

Sessions were organized in groups of eight talks, with an invited lecture of 30 minutes followed by seven submitted papers. Invited lectures have been compiled in two volumes entitled "Proceedings of the XX Colloquium Spectroscopicum Internationale and 7th International Conference on Atomic Spectroscopy" and is available from the Czechoslovak Spectroscopic Society of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia. Unlike in most meetings, all plenary lectures were held on the same day, and were led by a talk by Alan Walsh of CSIRO, Australia, on "Non-Dispersive Systems in Atomic Spectroscopy". Next, M.R. Aliev, of the U.S.S.R., spoke on "High-Resolution Vibration - Rotation Spectra of Molecules". J. Robin of France then stimulated a lively discussion with some comments on "What is the Fate of International Spectroscopic Conferences". V. Cermak of Czechoslovakia then delivered a lecture on "Electron Spectroscopy" and G.H. Morrison of Cornell University considered "Elemental Trace and Micro Analysis of Biological Materials". Finally, O. Brummer of the German Democratic Republic spoke on "Developments and Trends in Local (Micro) Analysis". Of these, the lectures by Walsh and Morrison are most germane to atomic spectroscopy and deserve further mention.

Walsh elaborated on a system first described in the Fifth International Conference on Atomic Spectroscopy in Melbourne Australia, in 1975. The system is extremely flexible and enables one to employ sputtering discharges (such as a Grimm discharge or hollow cathode lamp) or flames in a variety of ways, including their use as a primary source of radiation, as an atom cell for generating atomic vapor from sample material, or as a resonance monochromator. For

example, a nitrogen-separated air/acetylene flame could be used alternatively as an atom cell for atomic fluorescence spectrometry or as a resonance monochromator in atomic emission, absorption, or fluorescence. When used as a resonance monochromator, the separated flame serves to isolate a desired spectral line from all other background radiation falling upon it. A detector (generally a solar-blind photomultiplier), placed at an angle of  $90^\circ$  from radiation being directed onto the flame, detects only radiation capable of being absorbed and re-fluoresced by the flame. Therefore, the flame serves as a monochromator which is specific for the resonance spectral lines of whatever atoms reside within the flame. In turn, because the atoms residing in the flame can be varied merely by changing the identity of an aspirated and nebulized solution, the flame resonance monochromator is both versatile and selective.

In the talk by George Morrison, the importance of trace elements in biological materials was underlined and methods currently available for the analysis of such trace metals were compared. These methods included atomic absorption spectrometry (AAS), electrothermal AAS, emission spectroscopy (e.g. dc arc or spark spectroscopy), inductively coupled plasma atomic emission (ICP), instrumental neutron activation analysis (NAA), spark source mass spectrometry (SSMS), and x-ray fluorescence (XRF). Morrison pointed out that most trace elements now known to be essential were not realized to be important as recently as seven years ago. Moreover, many of these same elements are toxic when given in larger doses; consequently, the importance of accurate, rapid, inexpensive trace element analysis is becoming increasingly important. Unfortunately, no single technique provided sufficiently high sensitivity for all elements now known to be important. Overall, electrothermal atomization AAS provided the best compromise of high sensitivity, acceptable accuracy and precision, and low instrumental cost. Unfortunately, this technique is in-

herently slow and could determine only one element at a time, making it somewhat unattractive. In addition, the high cost and limited application to other biological materials than blood serum makes the inductively coupled plasma technique somewhat unappealing. Nonetheless, Morrison felt that these two techniques, with further development, would likely be the methods of choice for the determination of elements in biological matrices. Other emerging techniques, such as microwave-induced plasma (MIP) spectrometry could alter the picture in the future, however.

In the balance of the principal part of the congress, several trends seemed evident. One approach which seemed to gain momentum is the coupling of atomic absorption spectrometry and plasma spectrometry with separations techniques such as liquid and gas chromatography. Such a combination enables one to determine not only which elements are present in a sample but also to determine the state of such elements or in what compounds they are bound. Speciation of this kind is becoming increasingly important in clinical studies, environmental endeavors, and in other areas; we are likely to see increasing effort along these lines in the future.

Another technique which appeared to be gaining momentum is Zeeman-modulation atomic absorption spectrometry. In this method, a magnetic field is used to split the atomic spectral lines in either a source lamp or in the atoms generated from a sample into components which are polarized perpendicularly to each other. By employing a rotating polarizer, it then becomes possible to resolve the fine structure induced by the magnetic field. If such splitting is induced in the sample atoms, and if one of the resulting spectral components lies in the original location of the spectral line while the other, perpendicularly polarized component is shifted, it becomes possible to perform background correction much more exactly than with any other technique. Background

correction is required in many analyses because of the non-specific (molecular) absorption produced by some samples or by scattering of source radiation. In the Zeeman technique, shifting of the analyte atoms' spectral lines from their original location enables the background absorption to be monitored at that location, with no error introduced by absorption of the atoms themselves. Overall, the technique appears to be simple to implement and relatively inexpensive to install in conventional atomic absorption equipment.

Two other trends which are evident and which will be underscored by comments to be made in the following paragraphs are the entrenchment of electrothermal atomization techniques into atomic absorption spectroscopy and the continued increase in enthusiasm over plasma sources. Although atomic spectroscopists are becoming cognizant of the pitfalls of electrothermal atomization, the sensitivity, convenience, and small sample requirements of the technique override these objections. In the area of inductively coupled plasmas, one of the primary endeavors is toward understanding the plasma and reducing its cost. In efforts to reduce the plasma's cost, attempts are being made to use lower powers, to employ more efficient plasma torches, and to reduce the plasma's cooling gas (argon) requirements. Microwave-induced plasmas were also in evidence and their practicality was emphasized by the introduction of a commercial MIP system by a firm called EDT Research, located in the United Kingdom. In the following paragraphs, several papers highlighting these trends will be discussed briefly. Because of space and time requirements, a comprehensive coverage of the conference proceedings will not be attempted; rather, specific lectures will be mentioned which appeared to offer novel insights, unusual depth of understanding, or which opened up new areas of interest to atomic spectroscopists.

In paper #97, Professor C.Th.J. Alkemade discussed some of his recent work on lasers and flames. In particular, recent investigations on the saturation of atomic transitions was outlined and the influence of the temporal characteristics of the saturation process was emphasized. When a relatively long (microseconds) exciting laser pulse is employed, fluorescence generated under conditions of near-energy-level saturation exhibited a decay which was attributed to ionization of the fluorescing atoms. Addition of oxygen to the flame increased the effect and it was postulated that other species having high electron affinities would produce the same behavior. When this behavior exists, a plot of fluorescence intensity vs. incident source power does not level off as predicted by ordinary saturation theory, but continues to increase. Another interesting observation is that the apparent excitation spectrum of atoms obtained under saturation conditions is significantly broadened, the reason for such broadening being that saturation at the peak of the spectral line occurs first and reaches a limiting value while fluorescence at the wings of the line continues to increase, leading to an apparently broadened profile. In another interesting study, Alkemade's group examined level mixing which occurs upon two-photon excitation in sodium. A number of excitation transitions were induced by a two-photon process and fluorescence was observed from almost every state which was examined. This unexpectedly high degree of level mixing could explain the surprisingly high incident source power which is required to saturate many atomic transitions.

In paper #3, Paul Boumans and coworker deBoer addressed the question of ionization in an inductively coupled plasma. Such plasmas exhibit both high electron and ion concentrations but a relatively low susceptibility to ionization interferences. Moreover, the ratio of ions to atoms in such



a plasma is 1-3 orders of magnitude higher than would be predicted by a model based on local thermodynamic equilibrium. According to Boumans, these observations can be explained by viewing argon metastable atoms both as ionizers and ionizants. That is, the high energy (11.55 - 11.72 eV) of metastable argon is below the ground state energy (15.75 eV) of an argon ion. Therefore the argon metastable energy is high enough to ionize many atoms through collisions (i.e. Penning ionization), but is also capable of being thermally ionized itself. Because the predicted concentration of argon metastable ions in an ICP is high ( $10^{14}$  per cubic centimeter), it could play a dominant role in determining the overall ion concentrations in the plasma and might account for the unexpectedly high ion concentrations.

In two papers dealing with torch design and operation in an ICP, R.M. Barnes (paper #7) and Kornblum and deGalan (paper #8) found that ICP torches could be operated at relatively low gas flows and input powers, simply by slightly modifying the torch. Through theoretical modelling, Barnes found that an increased cooling gas swirl velocity should reduce pressure in the discharge and thereby require less coolant gas flow. Accordingly, the inlet tube for coolant gas was constricted and placed at an angle to increase the swirl velocity. With this modification, the linear coolant velocity was between 8 and 10 meters per second at a flow of 5 liters per minute; at a central (aerosol entry) flow velocity of 50-60 meters per second, the torch could be operated at 0.95 kilowatts, whereas a central velocity of 30 meters per second required only 0.5 kilowatts. Kornblum and de Galan discovered that an increase in the central tube channel length (where aerosol is introduced) made the central gas flow more laminar and narrower in its velocity profile, resulting in a better penetration of the plasma by aerosol species. This modified central tube was placed 2 millimeters below the lip

of the adjacent concentric quartz tube. With this modification, the greatest signal was found at the lowest operable central flow and at low (0.5 kilowatts) input power. However, the greatest line-to-background ratio was found at higher powers (1.5 kilowatts) and at relatively high central flows (2 liters per minute).

John C. Travis and his coworkers at the National Bureau of Standards described some of their recent work in opto-galvanic spectroscopy. This technique, whose name should perhaps be changed to something like photon-assisted ionization, was first described in Physical Review, volume 26, page 195 (1925). However, the NBS group was the first to attempt to exploit the phenomenon for analytical use. In the new configuration, two rods serving as electrodes were placed outside a flame and one centimeter above the burner top; a voltage is then applied between the rods (which are cathodic) and the burner top (which is grounded). When atoms are introduced into the flame in a manner identical to that employed in AAS, and a laser tuned to a spectral line of those atoms beamed through the flame, a change in current between the electrodes and the burner top is detected. Although Travis did not dwell on the mechanism of the phenomenon, it probably arises through thermally induced and photon-assisted ionization. That is, although some atoms will be thermally ionized in the flame anyway, the number of ions which are produced is increased by raising a substantial number of the atoms to higher energies through laser absorption. At present, use of this technique for analysis appears limited in scope because of high background ionization which exists in most flames and because of the large influence on ionization to be expected by concomitant elements in a typical sample. However, Travis indicated that a large number of transitions not commonly employed in atomic spectrometry can be used in opto-galvanic spectroscopy, making it possible to

employ a narrower range of laser wavelengths than would otherwise be required. This advantage is significant in laser spectroscopy, because of the limited wavelength range over which each dye can be employed in a typical laser.

In symposium 3 following the main congress, the dominant theme was the examination of atomization mechanisms in electro-thermal atomic absorption spectrometry. Unfortunately, most of the lectures which were presented contained only material which had been discussed before or was available in the open literature. In addition, most of the mechanisms which have been proposed are merely simple modifications of theories proposed earlier by B.V. L'Vov, and which are explained in detail and with clarity in his book (Atomic Absorption Spectroscopy, translated from the Russian and available from the National Technical Information Service, Springfield, Virginia 22151).

An interesting variant on the atomization mechanism theme was the paper presented by Leo de Galan (paper #542) who realized that the observed time behavior of atom concentration above an electrothermal atomizer can be described as a convolution of the atom supply rate (vaporization rate) and the atom removal rate. Accordingly, the two functions were separated and measured independently and the resulting convolution compared with observations. To measure the supply function, atoms were removed rapidly from the region above an electrothermal atomizer by rapidly flowing gas through the atomizer observation region. The atom removal function was obtained by stopping the gas flow and adding atoms to the observation region extremely rapidly (through flash volatilization of rapidly vaporizing elements such as mercury). For the supply function, these workers found that simple first order release kinetics don't accurately describe observations. Also, the removal rate is only a function of gas temperature, indicating that no wall process is involved

(at least for mercury). Although the resulting mathematical convolution of atom release and removal functions appear similar to observed atom concentration-time behavior, the approach is limited in scope. Specifically, atoms appear to have different removal functions, perhaps caused by changes in adsorption on the walls of the electrothermal atomizer. For example, the measured lead atom supply function, convoluted with a mercury removal function does not have the same appearance as the observed atom concentration vs. time plot. Work is proceeding to overcome this limitation. In an interesting final comment, de Galan noted that optimal results in the use of electrothermal atomizers would be obtained when the time constant for supply exactly equalled the time constant for release, a result which could be accomplished by heating an electrothermal atomization cell at a rate of approximately 1000 K per second and to use a tube (for a Varian CRA 63 system) which is 5 centimeters long and 4 millimeters inside diameter.

In perhaps the most innovative talk of the mini-symposium, Ray Woodruff (paper #544) described some recent work using a constant-temperature graphite furnace atomizer (appropriately termed the "Woodruff furnace"). With such an atomizer, the time required for atomization can be related to the total length of time required for a constant number of atoms to enter and depart the atom reservoir. To obtain the appropriate measurement, the observed time behavior of absorbance is measured and a line drawn across the resulting plot at a lower, fixed absorbance level. Because this absorbance represents a fixed atom concentration in the cell, the length of the drawn line can be unambiguously related to the atom cell's time constant. Moreover, because a single time constant implied loss of atoms through a diffusion process alone, a plot of the length of the straight line vs. sample weight should be linear. If such linearity is not observed, a sample loss mechanism other

than diffusion must be operative. In a related study, Woodruff and Marinkovic examined the migration of atoms vaporized from a constant-temperature furnace. In their measurements, such a furnace was operated in its normal way, but allowed to cool before atomization was complete. The tube was then cut into segments and the distribution of atoms along the length of the tube determined by conventional atomic absorption spectrometry. Woodruff postulated that this distribution, which was different from element to element, could be employed as a kind of "atom chromatography" (my term) and might enable one to overcome sample matrix interferences. Of course, the technique would not be applicable to elements such as silver and cadmium, which are lost primarily through diffusion rather than through absorption, although other elements such as potassium and aluminum could be separated readily.

Although the foregoing account is highly selective and provides only an overview of the proceedings and content of a prestigious international conference, further information is available in the articles cited earlier and from the individual authors. In addition, the author of the present article would be happy to supply further information, if it is desired.

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